STUDIES, RESEARCH AND INVESTIGATIONS

OF THE

OPTICAL PROPERTIES OF THIN FILMS OF METALS

SEMI-CONDUCTORS AND DIELECTRICS

SEVENTH

SEMI-ANNUAL REPORT

(August 16, 1962 - February 15, 1963)

Engineer Research and Development Laboratories

Contract No. DA-44-009-ENG-3828

Lawrence N. Hadley

Department of Physics

Colorado State University

Fort Collins, Colorado

TABLE OF CONTENTS

INTRODUCTION

Four more or less unrelated subjects have been under investigation during the past six months. Each has been the outgrowth of previous work, or is in some way related to it. These subjects are: 1) purity of chromium films reported on in the previous issue of this series; 2) use of a laser beam as an evaporating source, since this appears as a possible way of evaporating refractory materials; 3) smoothness of substrates -- a study necessary because of previous difficulties already reported on; and, 4) evaporation by means of electron bombardment -- again as a possible means of evaporating refractory materials.

PURITY OF CHROMIUM FILMS

Samples of evaporated chromium films (similar to those whose optical properties were discussed in the previous report of this series) were sent to the Consolidated Electrodynamics Corporation (CEC) for mass spectrographic analysis. The films were deposited on Float glass manufactured by Pilkington Bros., Ltd., of England. Deposition was made from a source consisting of 10 parallel 0.040" wires of commercial tungsten wire obtained from the General Electric Company. Evaporations were completed in times of 3 seconds or less. The impurity content of the tungsten wire and the analysis of the materials in the glass are not known. From analyses of chromium prepared in the same batch as that used (by the Albany Metallurgy Research Center of the U. S. Department of the Interior Bureau of Mines), it is estimated to contain the following impurities, in parts per million: 120 oxygen, 5 hydrogen, less than 20 nitrogen, 50 carbon, and trace amounts of aluminum, iron, silicon and nickel.

In a preliminary survey at CEC by Mr. J. McCleary, trace amounts (probably less than 10 ppm) were observed of Mn, Fe, Sn, Sb, and Cu.

Further work is under way to obtain a better analysis by using undoped tungsten wire (supplied by General Electric) as a source and evaporating chromium onto fused quartz substrates (supplied by Corning).

USE OF LASER BEAM AS EVAPORATING SOURCE

It has been suggested a number of times that the focused beam from a laser might be used as a possible evaporating source, since the energy may be focused onto an area which is approximately that of the Airy disc due to the diffraction limitation of the size of the laser rod. For a ruby laser operating at approximately 7000 Å and using a 0.6 cm diameter rod, the area of the Airy disc when the laser beam is focused is approximately $6 \times 10^{-8} cm^2$. Thus, even with imperfect focusing, very high energies per unit area can be achieved. If the energy in the flash can be absorbed by the material which is being irradiated, evaporation may result.

The thickness of an evaporated film is inversely proportional (approximately) to the product of heat of vaporization by density. Thus, assuming uniform evaporation to the half-sphere:

$$t = \frac{Q \times 10^8}{2\pi r^2 J H_v \rho}$$

where Q is the energy absorbed, in joules

r the distance between source and substrate

J is Joule's constant (4.18×10^3 joules/k cal)

H_v is the heat of vaporization in $\frac{\text{k cal}}{\text{gm}}$

ρ is the density in gm/cm^3

t is the thickness in Angstroms

The heat of fusion and the contribution due to change in temperature in the liquid phase have been neglected.

Values of the product $H_v\rho$ are shown in the accompanying chart. It will be noted that the refractory metals of interest have values ranging from 15-20 k cal/cm^3. Since the reflectivities of these materials are high, it will probably be necessary to use them in powdered form.

Calculations for tungsten indicate that with $r = 5$ cm one might expect a film thickness of approximately 8 Angstroms per joule absorbed. From data in Landolt-Bornstein the reflectivity of tungsten is close to 50% (at 6500 Å) and hence there is an expected thickness of 4Å/joule emitted.

$H_v \times \rho$

H																	HE
LI 2·48	BE 15·2												B 16·2	C 32·3	N	O	F	NE
NA 1·02	MG 2·32												AL 6·79	SI 3·36	P 0·17	S 0·19	CL	AR
K 0·42	CA 1·43	SC 5·40	TI 10·0	V 12·7	CR 10·1	MN 7·25	FE 11·9	CO 14·0	NI 13·8	CU 10·3	ZN 2·99	GA	GE 4·98	AS 0·59	SE 0·20	BR	KR
RB 0·32	SR 1·00	Y 4·68	ZR 8·54	NB	MO 13·6	TC	RU 17·8	RH 15·3	PD 11·5	AG 5·91	CD 1·84	IN 3·42	SN 4·31	SB 2·53	TE 0·58	I 0·20	XE
CS	BA 0·91	LA 4·26	HF 11·4	TA 16·5	W 19·4	RE 17·1	OS 19·3	IR 17·8	PT 13·4	AU 8·01	HG	TL 2·26	PB 2·34	BI 2·0	PO	AT	RN
FR	RA	AC															

CE 4·53	PR 3·73	ND 3·28	PM	SM 2·30	EN 1·45	GD 3·61	TB 3·63	DY 3·47	HO 3·55	ER 3·62	TN 3·32	YB 1·54	LU 3·04
TH	PA 868	U 9·14	NP	PU	AM	CM	BK	CF	ES	FM	MD	NO	LW

Product of Heat of Vaporization in kilocalories/$_{gm}$ by Density in $gm/_{cm^3}$

In an experimental arrangement using the figures given above, a total energy output (using manufacturer's data) of 30 joules gave a barely detectable film -- certainly much less than the 120 A expected. An electron micrograph showed a highly particulate structure with widely scattered clumps of the range 50 - 150 A in size. There was also some evidence of impact effect on the supporting collodian substrate as though each clump of tungsten had arrived at the substrate as a single pellet which then depressed the substrate for an appreciable area in the vicinity of the impact point. More work must be done here to verify this or establish it as artifact.

The above experiment made use of powdered tungsten. An earlier attempt using sheet tungsten gave no observable film, but the sheet tungsten showed damage from the radiation.

SMOOTHNESS OF SUBSTRATES

In several previous reports in this series mention has been made of an experimental difficulty which has arisen in the attempt to determine refractive index and extinction coefficient by measurement of reflectance, transmittance and thickness. The measured values, with the assignable error will not yield values of refractive index and extinction coefficient. For example, if the measured (corrected) transmittance value is located on the calculated curves of T vs s/λ for a particular n and k, the measured value of reflectance is always too low to fall on the corresponding calculated curve of R vs s/λ.

A possible source of this difficulty in the case of very thin metal films is the surface roughness of the substrate material. If the substrate is not molecularly smooth, then the deposited film will not be a plane slab with parallel sides, since the films have thicknesses of the order of 100 - 200 Å. The

calculated curves of R and T vs s/λ assume such geometry. In addition to the surface roughness of the substrate, there will inevitably be superposed the clump structure of the film itself.

From preliminary measurements, it is now believed that substrates previously used may have had a surface roughness of the order of 100 Å or more. New fused quartz substrates have just been received which were optically polished by Mr. Fred Pearson of the Rocky Mountain Scientific Instrument Company using special techniques.

An attempt to evaluate their surface roughness has been made by observing the "noise" on Fizeau interference fringes. Two such plates were selected which had surfaces flat (as contrasted to smooth) to better than λ Na/10 . These were then coated with silver to a transmission of 4% in a rapid evaporation. The plates were approximately one inch square. They were arranged such that there were only two fringes in

the surfaces under observation. Measurements were made with a traveling microscope of fringe width relative to fringe spacing. The fringe width was taken as the actual fringe line plus its associated noise due to surface roughness. Results on one such pair of surfaces yielded a fringe width of 35 $\pm$ 10 Å. Since the contribution to the noise is due to both surfaces, it appears that the plates are probably smooth to 20 Å or less.

Plate I shows typical photographs of the fringes. The photograph (a) shows fringes occurring between a polished plate of fused quartz of the type previously used in this work and one of the new plates discussed above. Measurements of fringe noise yield a surface roughness of 100-200 Å.

Photograph (b) shows fringes occurring between two plates of Corning fused quartz polished by Pearson. The double fringe is, of course, due to the Na line. Although the photograph is not an ideal example, it will be noted by comparison with (a) that the fringe noise is quite small.

(a) (b) (c)

PLATE I. Interference fringes between various polished quartz and film samples. See accompanying text for explanation.

The photograph (c) is shown for comparison. The lower quarts plate is again one of the Corning-Pearson samples, while the upper plate is one of the older quarts plates coated with TiO_2. The noise yields surface roughnesses of the order of 200-300 Å. Since the TiO_2 film was also this order of thickness, it is apparent that this roughness may have significantly influenced the results of the measurements of optical constants of TiO_2.

EVAPORATION BY ELECTRON BOMBARDMENT

Several types of electron bombardment heaters have been tried as high purity sources for the preparation of thin films. The first type of heater tried was a large carbon crucible, about 1" in diameter and ½" in height, mounted on a wire which was supported from a high voltage insulator. The crucible was then placed at a high positive potential (4000 volts). A 40 mil W filament at ground potential surrounded the crucible to act as an electron source. Currents of the order of 200 ma could be made to flow at around 500 volts. More power could not be put into the system because of a power supply maximum of 200 ma. No heating of the crucible was observed even though over a hundred watts was being put into the crucible. It is possible that many of the electrons were flowing to the wire rather than the crucible. Also, since the crucible was so large, a large amount of energy was required to raise its temperature appreciably.

A difficulty that arose here and in subsequent investigations was the problem of glow discharge in the vacuum system due to the presence of the high voltage. Glow discharge occurred only when the high voltage was on and the filament had been heated to just below its emitting temperature. When the glow discharge occurred, the pressure would rise rapidly and the current between the crucible and ground grew large. At this point the high voltage would have to be shut down until the vacuum had been restored in the chamber. By going through this procedure several times the chamber could be sufficiently outgassed to allow the experiment to be carried out.

A more suitable container was built to house the filament and target. It consisted of a can with a removable lid which also had a hole in it through which the vapor could pass. A hole was made in the bottom in which an insulator could be placed to support the crucible. Two insulators were provided inside the container to support the filament. However, this did not solve the problems of sagging filaments, melting insulators or low power input due to power supply limitations.

To solve the problem of melting insulators the crucible was mounted on a piece of 40 mil W wire about 2" long. The wire was clamped in a brass shank which was in turn mounted on a 2" insulator. The filament and power problems were solved by emission-limiting the current. This was done by making two sharp bends in the filament. In this way the heating of the filament could be localized in the bends, and could also be accurately controlled by regulating the filament current. Thus, the emission was held at a desired level allowing the voltage and hence the power to be varied over a wide range.

Under these conditions power input of the order of a kilowatt could be obtained. 0.5 grams of Al was evaporated in 1-2 seconds after the high voltage was turned on.

The crucible was replaced by a piece of 40 mil W wire. By carefully raising the voltage of the wire to 5000 volts and turning the filament current to maximum, the section of the wire in the same plane as the emission center of the filament could be melted. However, the molten tungsten ran

down the side of the wire so no evaporation took place. Another problem observed was that although the filament was heated for maximum emission, only 50-60 ma current could be obtained. It is possible that the density of electrons around the small plate was so great that space charge limitations had occurred.

To provide for better control the tungsten wire was suspended from above in an apparatus that could be raised and lowered manually from outside the vacuum chamber. In this way the tungsten wire could be adjusted so that just its tip lay in the plane of emission. Heating was then localized to the tip of the wire. The tip of the tungsten melted forming a small ball because of surface tension effects. After this occurred, the voltage could be raised to 7000 volts which caused more melting. By keeping the ball in the plane of emission it grew larger, which in turn allowed the current to increase. When the power had reached about 500 watts, the evaporation began with sparks flying in all directions. It continued as long as the target remained in the plane of emission.

None of the evaporated tungsten collected on a glass substrate, however. It did form a film on the metal substrate holder, which suggests that the vapor became charged as it left the source. Similar results were observed when evaporating a Mo wire, although only about one half as much power was required for the evaporation. In an attempt to eliminate the charged vapor, the source was placed at ground potential and the filament was placed at a high negative potential. The evaporation proceeded in the same manner, but again no film was collected on the substrate.

It was then suggested that if the vapor were passed through a cloud of electrons, the positively charged tungsten ions might collect the needed electrons, become neutral and stick to the substrate. This possibility has not been thoroughly investigated, but recent results indicate that it may be a solution to the problem.

Films of Al and Ag have been prepared using the electron bombardment technique. In these cases no ionization problems were encountered. This indicates that electron bombardment may be a method of producing high purity films of at least some materials.